

Data Evaluation Report on the aerobic biotransformation of fenpyroximate in water-sediment system

PMRA Submission Number {.....}

EPA MRID Number 45734202

Data Requirement: PMRA Data Code:
EPA DP Barcode: D285057
OECD Data Point:
EPA Guideline: 162-4

Test material:

Common name: Fenpyroximate

Chemical name

IUPAC: tert-Butyl (*E*)- α -[[[(1,3-dimethyl-5-phenoxy-1H-pyrazol-4-yl)methylene]amino]-*p*-toluate

CAS name: (*E*)-1,1-dimethylethyl 4-[[[[(1,3-dimethyl-5-phenoxy-1H-pyrazol-4-yl)methylene]amino]methyl]benzoate

CAS No: 134098-61-6

Synonyms: Benzoic acid, 4-[[[[(1,3-dimethyl-5-phenoxy-1H-pyrazol-4-yl)methylene]amino]oxy]methyl]-, 1,1-dimethylethyl ester, (*E*)-; AE F094552, Hoe 094552, AE B126265, ZK 126265; NNI-850.

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Company Code: [for PMRA]
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CITATION: Völkl, S. 1994. ¹⁴C-Fenpyroximate (NNI-850) [pyrazole-labelled] degradation and metabolism in aquatic systems. Unpublished study performed by RCC Umweltchemie Ag, Switzerland and submitted by Nihon Nohyaku Co. LTD, Japan. Study No.: RCC Project 346230. Experiment initiated August 10, 1993, and completed January 21, 1994 (p. 17). Final report issued November 16, 1994.

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EXECUTIVE SUMMARY

The aerobic biotransformation of [pyrazole-3-¹⁴C]-labeled tert-butyl (*E*)- α -[[[(1,3-dimethyl-5-phenoxy)pyrazol-4-yl)methylene]amino]-*p*-toluate (fenpyroximate) at 0.050 mg a.i./L was studied in a river water/sandy loam sediment system (initial surface water pH 8.31, initial organic carbon 1.7 mg/L; initial sediment pH 7.27, organic carbon 0.74 g C/100 g dry soil) from Switzerland; and a pond water/silt loam sediment (initial surface water pH 7.67, initial organic carbon 3.7 mg/L; initial sediment pH 6.89, organic carbon 4.41 g C/100 g dry soil) from Switzerland. The systems were incubated for 105 days in darkness at 20 \pm 2°C. The water/sediment ratio for the river and pond water sediment systems were approximately 550 mL of water to 220- 240 g wet sediment (2.3-2.5:1; v:w), respectively. This experiment was conducted in accordance with BBA Guidelines for Registration of Pesticides, Section IV:5-1, December 1990, and in compliance with USEPA GLP standards (1989). The test system consisted of glass metabolism flasks containing treated water/sediment ventilated with humidified air. Volatiles were trapped by passing outgoing air through trapping solutions of 2N NaOH and ethylene glycol in series. Test systems were equilibrated for approximately 4 weeks (22 days), treated, and duplicate samples collected at 0, 0.25, 1, 2, 7, 14, 30, 61, and 105 days posttreatment. Sterile control test systems were also utilized and sampled at 2, 61, and 105 days. Water was sampled by pipette without disturbing the sediment and aliquots analyzed by LCS directly; additional aliquots of water were extracted 1-3 times with ethyl acetate and once with acidified ethyl acetate. Sediment samples were extracted up to three times with methanol and 1-2 times with methanol:water (80:20, v:v) by shaking, and once with methanol by Soxhlet extraction. Water and sediment extracts were analyzed by LSC and TLC. Identification was based on comparison to reference standards. Analysis to confirm results was not performed. Portions of extracted sediments were analyzed by LSC following combustion.

At the time of treatment in the river and pond water/sediment systems, redox potentials in the water phase ranged from 214-220 mV, and in the sediment phase from -224 to -309 mV; oxygen content ranged from 4.7-5.0 mg/L, and pH was 8.38-8.55. Redox potential in the water phase remained >0, ranging from 128-239 mV through 105 days; however redox potentials in the sediment phase remained <0, ranging from -100 to -270 mV through 105 days. During the study, pH ranged from 7.68-8.57, and oxygen concentrations ranged from 2.5-7.8 mg/L. Microbial biomass in the river sediment at days 0 and 105 was 51.6 and 61 mg C/100 g dry soil, respectively. In the pond sediment, microbial biomass was 256.0 and 214.5 mg C/100 g dry soil, respectively.

The overall recovery of radiolabeled material from [¹⁴C] fenpyroximate in the total river and pond water/sediment system averaged 101.3 \pm 3.7% (range 93.8-108.9%) and 99.8 \pm 2.8% (range 92.7-103.9%) of the applied, respectively. The sediment:water ratios were approximately 1:0.8 immediately after treatment, 1:6.2 at day 7, and 1:2.6 at 105 days in the river water/sediment system; and 1:0.6 immediately after treatment, 1:2.8 at day 7, and 1:4.2 at 105 days in the pond water/sediment system.

In the total river water/sediment system, [¹⁴C]fenpyroximate averaged 98.0 to 102.0% of the applied at 0 through 2 days posttreatment, then decreased to 95.9% at 7 days, 51.0% at 30 days, and 21.8% at 105 days (study termination). [¹⁴C]Fenpyroximate was primarily associated with the sediment by 7 days

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posttreatment, and was not detected in the water beginning at 30 days. Three major transformation products were isolated: M11 (RW1/RS1; 1,3-dimethyl-5-phenoxyprazole-4-carbonitrile), M8 (RW6/RS2; 1,3-dimethyl-5-phenoxyprazole-4-carboxylic acid), and RW7. In the entire system, M11 averaged a maximum of 22.4-24.9% of the applied (8.0-8.8% in water, 13.6-16.8% in sediment) at 61-105 days posttreatment. M8 averaged a maximum of 18.1-18.8% of the applied (15.6-16.7% in water, 1.5-2.6% in sediment) at 30-105 days. RW7, which was not identified, averaged a maximum of 13.2% of the applied in the water at 14 days; because of the study author's coding system, it could not be determined if RW7 was present in the sediment. Eight minor transformation products were isolated from the water and four from the sediment. These compounds were not identified. Since the study author did not attempt to correlate unidentified compounds in the water with those in the sediment, it was not certain if these represent twelve different compounds or if some compounds were present in both media. No single unidentified compound in the water averaged >0.6% of the applied. In the sediment, RS5 averaged a maximum of 6.9% of the applied and other unidentified compounds were ≤3.3%. Extractable [¹⁴C]residues in the sediment increased from 42.7% of the applied at day 0 to a maximum of 87.5% at 7 days, before decreasing to 46.9% at 105 days. Nonextractable [¹⁴C]residues averaged a maximum 22.7% of the applied at 105 days posttreatment. At 105 days posttreatment, ¹⁴CO₂ totaled 2% of the applied and volatile organics were <0.1%.

In the total pond water/sediment system, [¹⁴C]fenpyroximate averaged 93.4 to 99.1% of the applied at 0 through 2 days posttreatment, then decreased to 66.0% at 14 days posttreatment, 37.8% at 30 days, and 15.8% at 105 days. [¹⁴C]Fenpyroximate was primarily associated with the sediment by 7 days posttreatment, and was not detected in the water beginning at 30 days. Five major transformation products were isolated: M11 (PW1/PS1), M8 (PW3/PS3), PS4, PW5, and PS6. In the entire system, M11 averaged a maximum of 30.4% of the applied (6.1% in water, 24.3% in sediment) at 105 days posttreatment. M8 averaged a maximum of 30.2% of the applied (27.8% in water, <4.8% in sediment) at 61 days. PW5, which was not identified, averaged a maximum of 20.8% of the applied in the water at 14 days. PS4 and PS6 were detected at 10.2 and 16.5% of the applied, respectively, in the sediment from one of the two samples collected at 30 days. Four minor transformation products were isolated from the water and five from the sediment. These compounds were not identified. No single unidentified compound in the water averaged >0.6% of the applied or in the sediment averaged >4.4%. Extractable [¹⁴C]residues in the sediment increased from 39.7% of the applied at day 0 to a maximum of 69.0% at 7 days, before decreasing to 51.2% at 105 days. Nonextractable [¹⁴C]residues averaged a maximum 28.2% of the applied at 105 days posttreatment. At 105 days posttreatment, ¹⁴CO₂ totaled 1% of the applied and volatile organics were <0.1%.

In the total "sterile" river and pond water/sediment systems (which actually were not sterile but contained reduced populations of microorganisms), [¹⁴C]fenpyroximate decreased from 99.8-101.7% of the applied at 2 days to 91.2% in the river system and 69.5% in the pond system at 105 days. In the river system, no major transformation products were identified. In the pond system, the major transformation products were M11 and M8. M11 was a maximum of 12.4% of the applied (61 days) in the entire system, 4.2% of the applied in water (61 days), 8.2% of the applied in sediment (61 days). M8 at a maximum of 10.2% of the applied (105 days), 8.3% of the applied in water (105 days), 1.9% of the

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applied in sediment (105 days). Extractable [^{14}C]residues in the sediment were a maximum of 92.2% and 84.0% of the applied, respectively, at 105 days. Nonextractable [^{14}C]residues in the sediment were a maximum of 1.9% of the applied at 61 days. $^{14}\text{CO}_2$ and volatile organics totaled $\leq 0.1\%$ of the applied at 105 days.

Based on first-order linear regression analysis, [^{14}C] fenpyroximate dissipated from the entire river water/sediment system, water phase and sediment phase with a reviewer-calculated half-life of 33.3, 2.7 and 38.1 days, respectively. In the pond water/sediment system, fenpyroximate dissipated slightly faster from the entire system, water and sediment phases, with a reviewer-calculated half-life of 19.9, 2.8 and 20.8 days, respectively. The linear upper 90th confidence bound on the mean for the entire systems is 68.9 days. The non-linear entire system half-lives for river and pond were 28.4 and 23.4 days, respectively. The non-linear upper 90th confidence bound on the mean for the entire systems is 41.7 days.

A metabolism pathway is proposed by the study author, in which [^{14}C]fenpyroximate degrades to M11 and then M8, with approximately 25% of the applied bound by 105 days in river and pond residues, respectively, and <2% radioactivity lost by volatilization.

Results Synopsis:

Test system: River water: sandy loam sediment system.

Half-lives of parent fenpyroximate:

Entire system (2-61 days): 33.3 days ($r^2 = 0.91$, $F=83$, $p=1.7\text{e-}5$).

River water (0-7 days): 2.6 days ($r^2 = 0.93$, $F=102$, $p=7.8\text{e-}6$).

Sediment (7-61 days): 38.1 days ($r^2 = 0.89$, $F=50$, $p=4\text{e-}4$).

Non-Linear Half-lives of parent fenpyroximate:

Total System (0-61 days): 28.4 days ($r^2 = 0.91$, $F=86$, $p<1\text{e-}4$).

Major transformation products:

M11 (RW1/RS1; 1,3-dimethyl-5-phenoxyprazole-4-carbonitrile).

M8 (RW6/RS2; 1,3-dimethyl-5-phenoxyprazole-4-carboxylic acid).

RW7.

Minor transformation products:

No minor transformation products were identified.

Test system: Pond water: silt loam sediment system.

Half-lives of parent fenpyroximate:

Entire system (0-61 days): 19.9 days ($r^2 = 0.97$, $F=420$, $p=7.6\text{e-}12$).

Pond water (2-14 days): 2.8 days ($r^2 = 0.99$, $F=372$, $p=4.3\text{e-}5$).

Sediment (7-61 days): 20.8 days ($r^2 = 0.93$, $F=86$, $p=9\text{e-}5$).

Non-Linear Half-lives of parent fenpyroximate:

Total System (0-105 days): 23.4 days ($r^2 = 0.96$, $F=403$, $p<1\text{e-}4$).

Major transformation products:

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M11 (PW1/PS1; 1,3-dimethyl-5-phenoxyprazole-4-carbonitrile).

M8 (PW3/PS3; 1,3-dimethyl-5-phenoxyprazole-4-carboxylic acid).

Minor transformation products:

No minor transformation products were identified.

Study Acceptability: This study is classified as acceptable. It is scientifically valid, but EFED notes that the sediment phase was anaerobic at the time of treatment and remained anaerobic throughout the study. A stratified system with negative redox potentials in soil and positive redox potentials in water is common in aerobic aquatic metabolism studies because soil has more buffering capacity than water. Also, all compounds present at >10% of the applied were not identified. However, the pattern of degradation is clear when the results of this study are compared to the anaerobic aquatic metabolism study. Similar metabolites were formed because of the negative redox potential of the soil in both studies. The only difference is that the M3 metabolite (hydroxylated parent minus tertiary butyl) degraded faster in the aerobic than in the anaerobic aquatic metabolism study.

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I. MATERIALS AND METHODS

GUIDELINE FOLLOWED: The study was conducted according with BBA Guidelines for Registration of Pesticides, Section IV:5-1, December 1990 (p. 21). Significant deviations from USEPA Subdivision N Guideline §162-4 were:

The sediment phase was anaerobic at the time of treatment and remained anaerobic throughout the study. This does not affect the validity of the study.

Four compounds present at >10% of the applied were not identified. RW7 was isolated at 13.2% of the applied from two samples, PW5 was isolated at 20.2 and 21.3% from two samples, and PS4 and PS6 were isolated from individual samples at 10.2 and 16.5% of the applied, respectively. This does not affect the validity of the study.

COMPLIANCE: This study was conducted in compliance with USEPA, OECD and Swiss Good Laboratory Practices (p. 18). Signed and dated No Data Confidentiality, GLP, and Quality Assurance statements were provided (pp. 2, 3 and 5). A Certificate of Authenticity was not provided.

A. MATERIALS:

1. Test Materials: [Pyrazole-3-¹⁴C]fenpyroximate (p. 23).

Chemical Structure:

Description: Off-white solid (p. 22).

Purity: Radiochemical purity: 99.0% (p. 23).
Batch/Lot No.: CP-1609.
Analytical purity: Not reported.
Specific activity: 21.8 mCi/mMol; 51.6 µCi/mg.
Location of radiolabel: 3-Carbon of the pyrazole ring.

Storage conditions of

test chemicals: The test material was stored in the dark in the freezer (-20°C; p. 22).

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Table 1: Physico-chemical properties of fenpyroximate.

Parameter	Values	Comments
Molecular weight:	421.5 g/mol	
Molecular formula:	$C_{24}H_{27}N_3O_4$	
Water solubility:	14.7×10^{-3} mg/L at 20°C	Other solubilities at 25°C: methanol: 15.1 g/L acetone: 154 g/L chloroform: 1218 g/L
Vapor pressure/volatility:	5.6×10^{-8} mm Hg at 25°C	
UV absorption:	Not reported.	
pK _a :	Not reported.	
K _{ow} /log K _{ow} :	Not reported.	
Octanol/water partition coefficient (log P _{ow}):	5.01	
Stability of compound at room temperature:	>2 years in a closed container away from heat	

Data obtained from p. 22 of the study report.

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2. Water-sediment collection, storage and properties:

Table 2: Description of water collection and storage.

Description		Details
Geographic location:	Water:	River: Mumpf Zeltplatz, Aargau/Switzerland. Pond: Weiherhof-Tal (Ormalingen, Baselland/Switzerland).
	Sediment:	River: Mumpf Zeltplatz, Aargau/Switzerland. Pond: Weiherhof-Tal (Ormalingen, Baselland/Switzerland).
Pesticide use history at the collection site:		Not reported.
Collection Date:		August 10, 1993.
Collection procedures:	Water:	Water was sampled with a plastic container.
	Sediment:	Sediment was sampled with a shovel.
Sampling depth:	Water:	10-30 cm.
	Sediment:	Top 5-10 cm of each system, at a location 1 to 2 m from shore.
Storage Conditions:		The water and sediment were stored at room temperature until sieving and thereafter at 4°C until flasks established.
Storage Length:		Not reported.
Preparation:	Water:	0.2 mm sieve.
	Sediment:	2 mm sieve.

Data obtained from p. 25 of the study report.

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Table 3: Properties of the water.

Property	River	Pond
Temperature (°C):	Surface: 20.0°C 5 cm above sediment: 20.0°C	Surface: 12.7°C 5 cm above sediment: 11.8°C
pH:	Surface: 8.31 5 cm above sediment: 7.74	Surface: 7.67 5 cm above sediment: 7.55
Redox potential (mV):	Surface: 211 5 cm above sediment: 193	Surface: 102 5 cm above sediment: 38
Oxygen content mg/L	Surface: 7.8 5 cm above sediment: 7.4	Surface: 8.9 5 cm above sediment: 4.8
Total Organic Carbon (mg/L):	1.7	3.7
Hardness (°dH):	11	18.5
Electrical conductivity (µS/cm):	Not reported.	Not reported.
Suspended solids (mg/L):	Not reported.	Not reported.
Biomass (mg microbial C/100 g, CFU or other):	Not reported.	Not reported.

Data obtained from Table 2, p. 56 of the study report.

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Table 4: Properties of the sediment.

Property	River	Pond
Textural classification (USDA):	Sandy loam	Silt loam
% sand:	61.0	37.7
% silt:	32.3	59.6
% clay:	6.7	2.7
pH (KCl):	7.27	6.89
Redox potential (mV):	-154	-78
Organic carbon (g C/100 g dry soil):	0.74	4.41
Organic matter (%):	Not reported.	Not reported.
CEC (mVal N/100 g dry soil):	8.7	8.9
Bulk density (g/cm ³):	Not reported.	
Biomass (mg microbial C/100 g):	51.6	256.0
Other:	Microbial biomass in the sediment was determined using a modification of the respiratory method.	

Data obtained from p. 26; Table 3 p. 57 of the study report.

B. EXPERIMENTAL CONDITIONS:

1. Preliminary experiments: Preliminary experiments were not conducted.

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2. Experimental conditions:

Table 5: Study design.

Criteria		Details
Duration of the test:		105 days.
Water: Filtered/unfiltered water: Type and size of filter used:		Filtered. 0.2 mm mesh sieve.
Amount of sediment and water/treatment:	Water:	550 mL corresponding water.
	Sediment:	River: 240 g wet sediment plus approximately 550 mL of water. Pond: 220 g sediment plus approximately 550 mL of water.
Water/sediment ratio:		River: 2.3:1 Pond: 2.5:1
Application rate:		Actual: 26.4 µg/sample, equivalent to 149.4 g a.i./ha. Nominal: 0.050 mg a.i./L
Control conditions, if used:		Water/sediment samples were prepared as described, sterilized by autoclaving twice prior to treatment, then incubated as described for the parent.
No. of Replications:	Controls, if used:	None; a single flask was collected at each interval.
	Treatments:	Duplicate flasks removed at each system at each sampling interval.
Test apparatus (type/material/volume):		Glass metabolism flasks (1-L, id 10.6 cm) filled with sediment to a height of 2 cm and sufficient water to achieve a column height of 6 cm (530 ml water) were attached to individual volatile trapping systems. The flasks were "ventilated" with moistened air, and a magnetic stirrer was used to gently agitate the water without disturbing the sediment. From this diagram, it appears that the air was bubbled into the water layer.
Details of traps for CO ₂ and organic volatiles, if any:		Humidified air was forced continuously through the sample flask (60-80 mL/minute), then through one 2N NaOH and one ethylene glycol (50 mL each) trapping solutions. The volatile trapping system is illustrated in Scheme 1, p. 93.
If no traps were used, is the system closed/open?		Volatiles traps were used.
Identity and concentration of co-solvent:		Acetone, <0.1% by volume (0.42 mL/approximately 780 g).

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Criteria		Details
Test material application:	Vol. of test solution used/treatment:	420 µL/sample.
	Application method:	Applied drop-wise to each sample of the aquatic system using a Hamilton syringe.
Any indication of the test material adsorbing to the walls of the test apparatus?		Not reported.
Biomass (mg microbial C/100g) of control:		Not determined; the sterile controls were analyzed by plate count and reported to contain a "reduced population" (not further described).
Biomass (µg microbial C/g dry soil) of treated:		Initiation: 51.6 river sediment; 256.0 pond sediment Termination: 61.0 river sediment, 214.5 pond sediment
Experimental conditions:	Temperature (°C):	20 ± 2°C.
	Continuous darkness:	Yes.
Other details, if any:		The samples were equilibrated for about 4 weeks prior to treatment.

Data obtained from pp. 19, 26-28, 47; Table 3, p. 57 of the study report.

3. Aerobic conditions: A stream of humidified air was pumped through the water-sediment systems for 4 weeks prior to treatment. Based on the illustration of the test system, it appears that the air inlet was under the water surface (Scheme 1, p. 93). In addition, a magnetic stirrer was placed in the water layer so as not to disturb the sediment. The oxygen content of the water and the redox potential of the water and sediment were measured during the preincubation and at each sampling interval (Tables 4-7, pp. 58-63). On the day of treatment, the oxygen content of the water was 4.7-5.0 mg/L, the redox potentials in the water were 214-220 mV, and the redox potentials in the sediment ranged from -224 to -309 mV (Table 6, p. 61; Table 7, p. 63). Therefore, on the day of treatment, the water environment was mildly oxidizing and the sediment environment was reducing.

4. Supplementary experiments: In order to obtain sufficient material to characterize the transformation products, three additional flasks per system were treated with [¹⁴C]fenpyroximate at approximately five times the recommended field rate (0.253 ppm; pp. 19, 27). Samples were incubated as described with the low dose samples, and single flasks were collected and analyzed after 29, 61 and 105 days posttreatment (p. 29).

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5. Sampling:

Table 6: Sampling details.

Criteria	Details
Sampling intervals:	0, 0.25, 1, 2, 7, 14, 30, 61, and 105 days.
Sampling method:	Entire flasks were collected at each sampling interval.
Method of collection of CO ₂ and volatile organic compounds:	The trapping solutions were replaced at each sampling interval or were monitored weekly.
Sampling intervals/times for: Sterility check: Redox potential/other:	The sterility of the controls was checked at 2, 61, and 105 days posttreatment. Oxygen concentration and pH of the water phase, and the redox potentials of the water and sediment phases were measured at time 0 and each sampling interval. Microbial biomass was determined at the start and termination of incubation.
Sample storage before analysis:	The water and sediment were separated on the day of sampling. It was not stated if samples were stored prior to analysis.
Other observations, if any:	None.

Data obtained from pp. 29-30, 47 of the study report.

C. ANALYTICAL METHODS:

Separation of water and sediment: The water was removed from the sediment using a glass pipette without disturbing the sediment (p. 30). After separation from sediment (no further details), radioactivity was determined directly by LSC, with aliquots (up to 500 µL) analyzed directly by TLC (p. 30).

Extraction/clean up/concentration methods: Aliquots of the waster were analyzed directly using LSC and TLC (p. 30). Additional aliquots were extracted with ethyl acetate (1-3 times) and acidified ethyl acetate (pH 3, 1 time). The extracts were combined and concentrated under reduced pressure at 30-40°C. Aliquots of the extracts and the extracted water were analyzed using LSC; radioactivity remaining in the water after partitioning was <0.005 mg/L. Aliquots of the concentrated extracts were analyzed using TLC.

The sediment was sequentially extracted with methanol (1-3 extractions) by shaking on a mechanical shaker for 30 minutes, with methanol:water (80:20, v:v; 1-2 extractions) by shaking as described; and with methanol by Soxhlet-extraction for 16 hours (p. 30). Aliquots of the extracts were analyzed for total radioactivity using LSC. Aliquots of the methanol and methanol:water extracts (Steps 1 and 2) were combined and concentrated under reduced pressure at about 40°C. The concentrated extracts were analyzed using TLC. The Soxhlet extract contained only low amounts of radioactivity (<10 ppb) and was not analyzed further.

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Nonextractable residue determination: Following extraction, portions of the extracted sediment were air-dried, homogenized, analyzed using LSC following combustion (pp. 30-31).

Volatile residue determination: Aliquots of the NaOH and ethylene glycol solutions were analyzed for total radioactivity using LSC (p. 31).

Total ^{14}C measurement: Total radioactivity associated with the samples was determined by summing the radioactivity recovered from the water samples, sediment extracts, extracted sediment, and volatile trapping solutions (p. 43).

Derivatization method, if used: A derivatization method was not employed.

Identification and quantification of parent compound: Water and sediment extracts were analyzed by one- and two-dimensional TLC using silica gel plates (60 F₂₅₄, p. 32). The sample extracts were analyzed using two-dimensional TLC using n-hexane:toluene:diisopropylether (20:40:50, v:v:v; SS13) or n-hexane:ethylacetate (25:75, v:v; SS14) in the first direction, and toluene:dioxane:acetic acid (70:35:3.5, v:v:v; SS15) in the second direction. Areas of radioactivity were located using a linear analyzer (p. 33). Samples were cochromatographed with nonlabeled reference standards of fenpyroximate, M1, M3, M6, M7, M8 and/or M11 (Figures 14-28, pp 109-123; the reference standards were visualized under UV (254 nm). In addition, [^{14}C]residues in the water and soil extracts were separated using one-dimensional TLC on silica gel plates developed in SS13 or SS14 (p. 49). Areas of radioactivity were scraped from the plates and reanalyzed with nonlabeled reference standards; the reanalysis was done on RP-18 plates using methanol:water (Figure 30, p. 125; Figure 33, p. 128).

Identification and quantification of transformation products: Transformation products were separated, quantified, and identified using the TLC analyses as described for the parent.

Detection limits (LOD, LOQ) for the parent compound: The detection limit for LSC was 0.17 ppb (p. 38). The limit of determination was <0.17 ppb using sample sizes up to 10 mL for water or extracts and up to 5 g for sediment samples. The limit of detection for TLC in water and sediment was 0.087 $\mu\text{g/L}$ and 0.069 $\mu\text{g/L}$, respectively.

Detection limits (LOD, LOQ) for the transformation products: Detection and quantification limits were the same as those identified for the parent.

II. RESULTS AND DISCUSSION:

A. TEST CONDITIONS: In both the river and pond systems, the water was aerobic and the sediment was anaerobic at the time of treatment and throughout the study. In the river water, the oxygen concentrations ranged from 2.1 to 6.6 mg/L (lowest at 7 days posttreatment) and the redox potential ranged from 128 to 239 mV (lowest at 2 days; Table 6, pp. 60, 61). In the river sediment, the redox potentials ranged from -112 to -309 mV. In the pond water, the oxygen concentrations ranged from 4.3

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to 7.8 mg/L (lowest at 0.25 days posttreatment) and the redox potential ranged from 128 to 233 mV (lowest at 2 days; Table 7, pp. 62, 63). In the pond sediment, the redox potentials ranged from -111 to -269 mV. During the study, the pH of the treated river water was 7.59-8.48 and of the treated pond water was 7.88-8.53; the water tender to become more acidic after 1 day posttreatment (Tables 6 and 7, pp. 60-62). The temperature of the systems was reported to be $20 \pm 2^{\circ}\text{C}$; no supporting data were provided (p. 27).

B. MATERIAL BALANCE: In the river water/sediment system, the overall recovery of radiolabeled material averaged $101.3 \pm 3.7\%$ (range 93.8-108.9%) of the applied (Table 10, p. 66). The sediment:water ratio was approximately 1:0.8 immediately after treatment, 1:6.2 at day 7, and 1:2.6 at 105 days (reviewer calculated from water and sediment distribution data in Table 10, p. 66).

In the pond water/sediment system, the overall recovery averaged $99.8 \pm 2.8\%$ (range 92.7-103.9%) of the applied (Table 14, p. 70). The sediment:water ratio was approximately 1:0.6 immediately after treatment, 1:2.8 at day 7, and 1:4.2 at 105 days (reviewer calculated from water and sediment distribution data in Table 14, p. 70).

In the “sterile” control systems, overall recovery ranged 99.5-103.9% of the applied, respectively (Table 13, p. 69; Table 17, p. 73).

Table 7: Biotransformation of [^{14}C]fenpyroximate, expressed as percentage of applied radioactivity (mean \pm s.d.; n = 2), in river water/sediment system under aerobic conditions.

Compound		Sampling times (days)								
		0	0.25	1	2	7	14	30	61	105
Fenpyroximate	water	55.4 \pm 1.4	56.1 \pm 6.7	49.6 \pm 1.1	54.2 \pm 9.7	9.5 \pm 0.4	2.0 \pm 0.1	ND	ND	ND
	sediment	42.7 \pm 0.3	41.9 \pm 1.1	49.8 \pm 2.2	47.8 \pm 8.7	86.4 \pm 2.8	58.8 \pm 1.1	51.0 \pm 1.8	29.6 \pm 7.6	21.8 \pm 4.0
	entire system	98.1 \pm 1.3	98.0 \pm 7.9	99.4 \pm 1.1	102.0 \pm 1.0	95.9 \pm 2.4	60.7 \pm 1.1	51.0 \pm 1.8	29.6 \pm 7.6	21.8 \pm 4.0
RW1 (M11)	water	ND	ND	ND	ND	0.6 \pm 0.2	5.5 \pm 1.1	5.3 \pm 0.4	8.0 \pm 0.9	8.8 \pm 1.5
RS1(M11)	sediment	ND	ND	ND	ND	ND	1.8 \pm 0.6	6.8 \pm 0.4	16.8 \pm 3.0	13.6 \pm 1.6
RW6 (M8)	water	ND	ND	0.2 \pm 0.1	1.2 \pm 0.1	4.2 \pm 2.3	9.0 \pm 1.3	16.6 \pm 1.8	16.7 \pm 2.5	15.6 \pm 1.6
RS2 (M8)	sediment	ND	ND	ND	ND	ND	0.9 \pm 0.2	1.5 \pm 0.0	2.0 \pm 0.9	2.6 \pm 0.1
RW2	water	ND	ND	ND	<0.1	ND	ND	ND	ND	ND
RW3	water	ND	ND	ND	0.2 \pm 0.0	0.6 \pm 0.1	0.4 \pm 0.2	ND	ND	ND
RS3	sediment	ND	ND	ND	<0.6	1.1 \pm 0.1	1.6 \pm 0.3	ND	ND	ND
RW4	water	ND	ND	ND	<0.1	ND	ND	ND	ND	ND
RS4	sediment	ND	ND	ND	ND	ND	ND	2.7 \pm 2.5	3.3 \pm 1.5	<1.6
RW5	water	ND	ND	0.2	0.2 \pm 0.0	0.2 \pm 0.1	ND	ND	ND	ND
RS5	sediment	ND	ND	ND	<0.3	ND	ND	4.2 \pm 1.9	<6.6	6.9 \pm 1.9
RS6	sediment	ND	ND	ND	ND	ND	ND	<0.5	<0.7	1.2 \pm 0.1
RW7	water	ND	ND	ND	ND	ND	13.2 \pm 0.0	6.0 \pm 0.8	3.8 \pm 0.2	1.6 \pm 1.3
RW8	water	ND	ND	ND	ND	0.3 \pm 0.0	<0.1	<0.2	ND	0.1
RW9	water	ND	ND	ND	ND	ND	0.4 \pm 0.0	ND	<0.3	0.2 \pm 0.1
RW10	water	ND	ND	ND	ND	ND	ND	<0.1	<0.3	ND
RW11	water	ND	ND	ND	ND	ND	ND	ND	<0.3	ND

Compound		Sampling times (days)								
		0	0.25	1	2	7	14	30	61	105
¹⁴ CO ₂	entire system	ND	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.5 ± 0.14	1.95 ± 0.21
Volatile compounds	entire system	ND	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.2	<0.1
Extractable residues	sediment	42.7 ± 0.3	41.9 ± 1.1	49.8 ± 2.2	48.3 ± 8.8	87.5 ± 2.6	63.0 ± 1.1	66.2 ± 1.6	55.3 ± 1.8	46.9 ± 0.5
Nonextractable residues	sediment	0.8 ± 0.1	1.3 ± 0.1	2.0 ± 0.3	2.2 ± 0.7	5.8 ± 0.8	4.1 ± 0.2	8.2 ± 0.5	14.1 ± 2.1	22.7 ± 1.4
Total % recovery	water	55.4 ± 1.4	56.1 ± 6.7	49.9 ± 1.3	55.8 ± 9.5	15.0 ± 2.7	30.8 ± 2.8	27.9 ± 1.2	29.0 ± 1.2	26.3 ± 1.6
	sediment	43.5 ± 0.1	43.2 ± 1.1	51.8 ± 1.9	50.5 ± 9.5	93.3 ± 1.8	67.1 ± 0.8	74.4 ± 2.1	69.4 ± 0.3	69.6 ± 1.9
	entire system	98.9 ± 1.3	99.3 ± 7.8	101.7 ± 0.6	106.3 ± 0.0	108.2 ± 0.9	97.9 ± 1.9	102.4 ± 0.8	99.1 ± 0.6	97.8 ± 0.6

Means and standard deviations calculated by the reviewer using data from Table 10, p. 66; Table 18, p. 74, Table 19, p. 75; Table 23 p. 79 of the study report. Compounds in different media but identified by the same number do not necessarily represent the same compound; for example, RW6 in the water corresponds to RS2 in the sediment, rather than to RS6 in the sediment.

ND Not detected.

Table 8: Biotransformation of [^{14}C]fenpyroximate, expressed as percentage of applied radioactivity (mean \pm s.d.; n = 2), in pond water/sediment system under aerobic conditions.

Compound		Sampling times (days)								
		0	0.25	1	2	7	14	30	61	105
Fenpyroximate	water	59.4 \pm 6.7	51.6 \pm 1.8	51.5 \pm 3.4	64.8 \pm 9.7	14.6 \pm 0.4	3.1 \pm 0.1	<0.1	ND	ND
	sediment	39.7 \pm 8.4	41.8 \pm 3.7	42.7 \pm 8.2	33.6 \pm 8.0	67.2 \pm 6.3	63.0 \pm 0.6	37.7 \pm 16.4	11.8 \pm 1.8	15.8 \pm 3.5
	entire system	99.1 \pm 1.7	93.4 \pm 5.5	94.2 \pm 4.9	98.5 \pm 1.3	81.7 \pm 5.3	66.0 \pm 0.2	37.8 \pm 16.3	11.8 \pm 1.8	15.8 \pm 3.5
PW1 (M11)	water	ND	ND	ND	ND	0.4 \pm 0.2	1.9 \pm 0.1	3.7 \pm 0.4	6.4 \pm 0.8	6.1 \pm 0.6
PS1 (M11)	sediment	ND	ND	ND	ND	ND	1.0 \pm 0.1	6.1 \pm 0.4	18.6 \pm 4.3	24.3 \pm 4.5
PW2	water	ND	ND	ND	ND	0.3 \pm 0.1	0.1	0.2	ND	ND
PS2	sediment	ND	ND	ND	ND	ND	ND	0.2	ND	0.3 \pm 0.0
PW3 (M8)	water	ND	ND	ND	ND	<0.4	ND	8.9 \pm 2.7	27.7 \pm 2.6	12.4 \pm 2.4
PS3 (M8)	sediment	ND	ND	ND	ND	ND	0.4 \pm 0.1	2.6 \pm 0.4	<4.8	3.8 \pm 0.5
PW4	water	ND	ND	ND	ND	ND	0.5 \pm 0.0	ND	0.6	<0.3
PS4	sediment	ND	ND	ND	0.2 \pm 0.0	1.8 \pm 0.6	4.5 \pm 0.1	9.1 \pm 1.6	5.3 \pm 4.3	0.2
PW5	water	ND	ND	0.5 \pm 0.1	1.1 \pm 0.1	11.2 \pm 2.4	20.8 \pm 0.8	14.6 \pm 3.3	0.6 \pm 0.1	0.3 \pm 0.3
PS5	sediment	ND	ND	ND	ND	ND	ND	ND	<4.4	2.2 \pm 1.1
PW6	water	ND	ND	ND	ND	ND	ND	1.4	1.4 \pm 0.7	ND
PS6	sediment	ND	ND	ND	ND	ND	ND	<16.5	2.6	3.5
PW7	water	ND	ND	ND	ND	ND	ND	ND	0.5 \pm 0.4	ND
PS7	sediment	ND	<1.4	<0.1	ND	ND	ND	ND	ND	<0.4
PW8	water	ND	ND	ND	ND	ND	ND	ND	0.2 \pm 0.1	ND
PS8	sediment	ND	<0.5	ND	ND	ND	ND	<0.4	1.1 \pm 0.0	0.9 \pm 0.1

Compound		Sampling times (days)								
		0	0.25	1	2	7	14	30	61	105
¹⁴ CO ₂	entire system	ND	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.3 ± 0.1	1.0 ± 0.1
Volatile compounds	entire system	ND	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Extractable residues	sediment	39.7 ± 8.4	42.7 ± 2.3	42.8 ± 8.3	33.8 ± 8.1	69.0 ± 5.7	68.8 ± 0.7	64.1 ± 5.1	44.0 ± 3.6	51.2 ± 6.7
Nonextractable residues	sediment	1.2 ± 0.1	1.8 ± 0.7	2.3 ± 0.2	1.9 ± 0.4	6.4 ± 0.3	6.4 ± 0.1	7.3 ± 1.8	18.1 ± 0.2	28.2 ± 3.2
Total % recovery	water	59.4 ± 6.7	51.6 ± 1.8	52.0 ± 3.4	65.9 ± 6.6	26.8 ± 2.8	26.3 ± 0.9	28.8 ± 2.1	37.4 ± 3.6	18.9 ± 3.1
	sediment	40.9 ± 8.3	44.5 ± 3.0	45.1 ± 8.6	35.8 ± 8.4	75.4 ± 5.4	75.2 ± 0.8	71.4 ± 3.3	62.1 ± 3.4	79.4 ± 3.5
	entire system	100.4 ± 1.6	96.2 ± 4.9	97.0 ± 5.2	101.7 ± 1.8	102.2 ± 2.5	101.4 ± 0.1 ^a	100.2 ± 1.2 ^a	99.8 ± 0.5	99.3 ± 2.9

Means and standard deviations calculated by the reviewer using data from Table 14, p. 70; Table 27, p. 83, Table 28, p. 84; Table 32 p. 88 of the study report. Compounds in different media but identified by the same number do not necessarily represent the same compound; for example, RW6 in the water corresponds to RS2 in the sediment, rather than to RS6 in the sediment.

a Since the averages reported by the study author for the total recovery in the entire system (days 14 and 30) appear to be in error, the reviewer-calculated means were used.

ND Not detected.

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Table 9: Biotransformation of [^{14}C]fenpyroximate, expressed as percentage of applied radioactivity in “sterile” river water/sediment system under aerobic conditions.

Compound		Sampling times (days)		
		2	61	105
Fenpyroximate	water	55.3	5.7	4.1
	sediment	46.4	80.6	87.1
	entire system ¹	101.7	86.3	91.2
RW1 (M11)	water	ND	4.1	1.8
RS1 (M11)	sediment	ND	4.8	3.5
RW5	water	ND	2.7	3.7
RW6 (M8)	water	ND	0.8	1.0
RS2 (M8)	sediment	ND	ND	0.6
RS4	sediment	ND	ND	0.6
RS6	sediment	ND	ND	0.4
RW7	water	ND	0.1	0.4
$^{14}\text{CO}_2$	entire system	ND	<0.01	<0.1
Volatile compounds	entire system	ND	<0.01	<0.01
Extractable residues	sediment	46.4	85.3	92.2
Nonextractable residues	sediment	1.0	1.9	0.7
Total % recovery ¹	water	55.3	13.4	11.0
	sediment ²	47.4	87.2	92.9
	entire system	102.7	100.6	103.9

Single samples were collected at each sampling interval. Data obtained from Table 13, p. 69; Table 22, p. 78; Table 26, p. 82 in the study report. The study author reported that systems did not remain sterile, but that the populations of microorganisms were “reduced”.

1 The total percent of fenpyroximate in the entire system was calculated by the reviewer by summing the amount in water and sediment.

2 The total % recovered in the sediment was calculated by the reviewer by summing extractable and nonextractable residues.

ND Not detected.

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Table 10: Biotransformation of [^{14}C]fenpyroximate, expressed as percentage of applied radioactivity in “sterile” pond water/sediment system under aerobic conditions.

Compound		Sampling times (days)		
		2	61	105
Fenpyroximate	water	47.6	1.5	0.8
	sediment	52.2	72.5	69.5
	entire system ¹	99.8	74	70.3
PW1 (M11)	water	ND	4.2	2.3
PS1 (M11)	sediment	ND	8.2	7.8
PW3 (M8)	water	ND	6.5	8.3
PS3 (M8)	sediment	ND	1.0	1.9
PW4	water	ND	1.0	ND
PS4	sediment	ND	0.9	ND
PW5	water	ND	1.4	2.9
PS5	sediment	ND	0.6	3.0
RW7	water	ND	0.1	0.4
$^{14}\text{CO}_2$	entire system	ND	<0.01	<0.1
Volatile compounds	entire system	ND	<0.1	<0.1
Extractable residues	sediment	52.2	83.2	84.0
Nonextractable residues	sediment	<0.1	1.9	1.3
Total % recovery ¹	water	47.6	14.6	14.2
	sediment ²	52.2	85.1	85.3
	entire system	99.8	99.7	99.5

Single samples were collected at each sampling interval. Data obtained from Table 17, p. 73; Table 31, p. 87; Table 35, p. 91 in the study report. The study author reported that system did not remain sterile; reduced populations of microorganisms were present.

1 The total percent of fenpyroximate in the entire system was calculated by the reviewer by summing the amount in water and sediment.

2 The total % recovered in the sediment was calculated by the reviewer by summing extractable and nonextractable residues.

ND Not detected.

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C. TRANSFORMATION OF PARENT COMPOUND: In the total river water/sediment system, [^{14}C]fenpyroximate averaged 98.0 to 102.0% of the applied at 0 through 2 days posttreatment, then decreased to 95.9% at 7 days, 51.0% at 30 days, and 21.8% at 105 days (study termination; Table 18, p. 74). Immediately after treatment, 55.4% of the applied [^{14}C]fenpyroximate was associated with the water and 42.7% with sediment. At 7 days posttreatment, 9.5% of the applied was associated with the water and 86.4% with sediment. Beginning at 30 days, [^{14}C]fenpyroximate was undetected in the water.

In the total pond water/sediment system, [^{14}C]fenpyroximate averaged 93.4 to 99.1% of the applied at 0 through 2 days posttreatment, then decreased to 66.0% at 14 days posttreatment, 37.8% at 30 days, and 15.8% at 105 days (study termination; Table 27, p. 83). Immediately after treatment, 59.4% of the applied [^{14}C]fenpyroximate was associated with the water and 39.7% with sediment. At 7 days posttreatment, 14.6% of the applied was in water and 67.2% in sediment. Beginning at 30 days, [^{14}C]fenpyroximate averaged <0.1% in the water.

In the total “sterile” river and pond water/sediment systems, [^{14}C]fenpyroximate decreased from 99.8-101.7% of the applied at 2 days to 91.2% in the river system and 70.3% in the pond system at 105 days (Table 22, p. 78; Table 26, p. 82; Table 31, p. 87; Table 35, p. 91). The study author indicated that the sterile systems contained reduced populations of microorganisms, so that some biological degradation was occurring; no quantitative population data were provided (p. 47).

HALF-LIVES: Based on first-order linear regression analysis, [^{14}C] fenpyroximate dissipated from the entire river water/sediment system, water phase and sediment phase with a reviewer-calculated half-life of 33.3, 2.7 and 38.1 days, respectively. In the pond water/sediment system, fenpyroximate dissipated slightly faster from the entire system, water and sediment phases, with a reviewer-calculated half-life of 19.9, 2.8 and 20.8 days, respectively. The linear upper 90th confidence bound on the mean for the entire systems is 68.9 days. The non-linear entire system half-lives for river and pond were 28.4 and 23.4 days, respectively. The non-linear upper 90th confidence bound on the mean for the entire systems is 41.7 days.

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Table 8: Half-life ($t_{1/2}$)/DT₅₀ values for the biotransformation of fenpyroximate.

Media	First order Linear			DT ₅₀ (days)	DT ₉₀ (days)
	Half-life (days)	Regression equation	r ²		
River water/sediment system					
Entire system	2-61 day data: 33.3	y = -0.0208x + 4.5938	0.9117	27.6	248.0
Water	0-7 day data: 2.65	y = -0.2619x + 4.1713	0.9274	2.8	9.2
Sediment	7-61 day data: 38.1	y = -0.0182x + 4.4689	0.8933	ND	ND
Entire System (non-linear)	0-61 day data: 28.4	Y=-0.0244x + 104.9	0.91	ND	ND
Pond water/sediment system					
Entire system	0-61 day data: 19.9	y = -0.0348x + 4.6154	0.9678	24.3	126.7
Water	2-14 day data: 2.8	y = -0.2515x + 4.5863	0.9894	3.1	10.3
Sediment	7-61 day data: 20.8	y = -0.0334x + 4.5328	0.9346	ND	ND
Entire System (non-linear)	0-105 day data: 23.4	Y=-0.0296x + 98.7	0.96	ND	ND

Data obtained from pp. 38, 50; Table 19, p. 75; Table 23, p. 79; Table 28, p. 84; Table 32, p. 88 of the study report. Half-lives were calculated using all intervals of data. DT50 and DT90 calculated by the study author using first order, 1.5-order or second order kinetic model.

ND Not determined.

TRANSFORMATION PRODUCTS: In the river water/sediment system, three major transformation products were isolated: M11 (RW1/RS1; 1,3-dimethyl-5-phenoxyprazole-4-carbonitrile), M8 (RW6/RS2; 1,3-dimethyl-5-phenoxyprazole-4-carboxylic acid), and RW7 (Table 19, p. 75 and Table 23, p. 79). In the entire system, M11 averaged a maximum of 22.4-24.9% of the applied (8.0-8.8% in water, 13.6-16.8% in sediment) at 61-105 days posttreatment. M8 averaged a maximum of 18.1-18.8% of the applied (15.6-16.7% in water, 1.5-2.6% in sediment) at 30-105 days. RW7, which was not identified, averaged a maximum of 13.2% of the applied in the water at 14 days; because of the study author's coding system, it could not be determined if RW7 was present in the sediment. Eight minor transformation products were isolated from the water and four from the sediment. These compounds were not identified. Since the study author did not attempt to correlate unidentified compounds in the water with those in the sediment, it was not certain if these represent twelve different compounds or if some compounds were present in both media. No single unidentified compound in the water averaged >0.6% of the applied. In the sediment, RS5 averaged a maximum of 6.9% of the applied and other unidentified compounds were ≤3.3%.

In the pond water/sediment system, five major transformation products were isolated: M11 (PW1/PS1), M8 (PW3/PS3), PS4, PW5, and PS6 (Table 28, p. 84 and Table 32, p. 88). In the entire system, M11 averaged a maximum of 30.4% of the applied (6.1% in water, 24.4% in sediment) at 105 days

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posttreatment. M8 averaged a maximum of 30.2% of the applied (27.8% in water, <4.8% in sediment) at 61 days. PW5, which was not identified, averaged a maximum of 20.8% of the applied in the water at 14 days. PS4 and PS6 were detected at 10.2 and 16.5% of the applied, respectively, in the sediment from one of the two samples collected at 30 days. Four minor transformation products were isolated from the water and five from the sediment. These compounds were not identified. No single unidentified compound in the water averaged >0.6% of the applied or in the sediment averaged >4.4%.

In the “sterile” river water/sediment systems, no major transformation products were identified (Table 22, p. 78; Table 26, p. 82). In the “sterile pond water/sediment system, the major transformation product was M11, at a maximum of 12.4% of the applied (61 days) in the entire system, 4.2% of the applied in water (61 days), 8.2% of the applied in sediment (61 days); and M8 at a maximum of 10.2% of the applied (105 days), 8.3% of the applied in water (105 days), 1.9% of the applied in sediment (105 days; Table 31, p. 87; Table 35, p. 91).

NONEXTRACTABLE AND EXTRACTABLE RESIDUES: In the river system, extractable [¹⁴C]residues in the sediment increased from 42.7% of the applied at day 0 to a maximum of 87.5% at 7 days, before decreasing to 46.9% at 105 days (Table 10, p. 66). Nonextractable [¹⁴C]residues averaged a maximum 22.7% of the applied at 105 days posttreatment.

In the pond system, extractable [¹⁴C]residues in the sediment increased from 39.7% of the applied at day 0 to a maximum of 69.0% at 7 days, before decreasing to 51.2% at 105 days (Table 14, p. 70). Nonextractable [¹⁴C]residues averaged a maximum 28.2% of the applied at 105 days posttreatment.

In the “sterile” river and pond water/sediment systems, extractable [¹⁴C]residues in the sediment were a maximum of 92.2% and 84.0% of the applied, respectively at 105 days (Table 13, p. 69; Table 17, p. 73). Nonextractable [¹⁴C]residues in the sediment were a maximum of 1.9% of the applied at 61 days.

VOLATILIZATION: At 105 days posttreatment in the river and pond systems, ¹⁴CO₂ totaled 1-2% of the applied and volatile organics were <0.1% (Table 10, p. 66; Table 14, p. 70). In the “sterile” systems, ¹⁴CO₂ and volatile organics totaled ≤0.1% of the applied at 105 days (Table 13, p. 69; Table 17, p. 73).

TRANSFORMATION PATHWAY: A metabolism pathway is illustrated in Scheme 3, p. 95. [¹⁴C]Fenpyroximate degrades to M11 and then M8, with 22.7% and 28.2% of the applied in bound river and pond residues, respectively, by 105 days, and <2% of the applied lost by volatilization (Table 13, p. 69; Table 17, p. 73).

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Table 9: Chemical names for transformation products of fenpyroximate in aerobic river or pond water.

Applicant's Code	CAS Number	Chemical Name	Chemical formula	Molecular weight (g/mol)	SMILES string
M11 (RW1,RS1;PW1,PS1)	-	1,3-Dimethyl-5-phenoxyprazole-4-carbonitrile	-	-	-
M8 (RW6, RS2; PW3, PS3)	-	1,3-Dimethyl-5-phenoxyprazole-4-carboxylic acid	-	-	-

Data were obtained from p. 128b; Table 19, p. 75, Table 23, p. 79, Table 28, p. 84, Table 32, p. 88 of the study report.

- Not reported.

D. SUPPLEMENTARY EXPERIMENT-RESULTS: In the river water/sediment system high dose samples, the overall radioactive recovery ranged from 99.7-102.4% of the applied (Table 12, p. 68). [¹⁴C]Residues in water and sediment were 38.8% and 63.5% of the applied, respectively at day 29, and 37.5% and 60.8%, respectively at 105 days (total [¹⁴C]residues in the sediment were reviewer-calculated by summing extractable and nonextractable sediment). Extractable [¹⁴C]residues were 57.2% of the applied at day 29 and 47.7% at 105 days (reviewer-calculated sum of sediment extractables and Soxhlet extraction). Non-extractable [¹⁴C]residues were 6.3% of the applied at 29 days and 13.1% at 105 days. Volatile organics and ¹⁴CO₂ were <2.0% of the applied at 105 days. [¹⁴C]Fenpyroximate was essentially undetected in water, reaching a maximum of 0.1% on day 61; in sediment [¹⁴C]fenpyroximate decreased from 36.4% of the applied at 29 days to 14.0% at 105 days (Table 21, p. 77; Table 25, p. 81). There were three major transformation products: M11 (RW1/RS1) was a maximum of 32.2% of the applied at 105 days (8.5% in water, 23.7% in sediment), M8 (RW6/RS2) was a maximum of 39.0% of the applied at 61 days (32.9% in water, 6.1% in sediment), RW7 was a maximum of 13.4% of the applied at 29 days in water. Nine minor transformation products were isolated in water and sediment, each at <5.0% of the applied.

In the pond river water/sediment system high dose samples the overall radioactive recovery ranged from 98.9-100.8% of the applied (Table 16, p. 72). [¹⁴C]Residues in water and sediment were 29.5% and 71.4% of the applied, respectively at day 29, and 33.2% and 65.1%, respectively at 105 days (total [¹⁴C]residues in the sediment were reviewer-calculated by summing extractable and nonextractable sediment). Extractable [¹⁴C]residues were 65.6% of the applied at day 29 and 52.3% at 105 days (reviewer-calculated sum of sediment extractables and Soxhlet extraction). Non-extractable [¹⁴C]residues were 5.8% of the applied at 29 days and 12.8% at 105 days. Volatile organics and ¹⁴CO₂ were <1.0% of applied at 105 days. [¹⁴C]Fenpyroximate was essentially undetected in water, reaching a maximum of 0.2% on day 61; in sediment [¹⁴C]fenpyroximate decreased from 24.5% of the applied at 29 days to 8.5% at 105 days (Table 30, p. 86; Table 34, p. 90). There were two major transformation products: M11 (PW1/PS1) was a maximum of 20.4% of the applied at 105 days (6.3% in water, 14.1% in sediment); M8 (PW3/PS3) was a maximum of 50.1% of the applied at 61 days (38.4% in water, 11.7% in sediment). Twelve minor transformation products were isolated in water and sediment, each at <5.0% of the applied.

III. STUDY DEFICIENCIES:

1. The sediment phases of both the river and pond systems were anaerobic at the time of treatment and remained anaerobic throughout the study. Redox potentials in the sediment were -224 to -309 mV at the time of application and remained <0mV, ranging from -100 to -270 mV through 105 days (Table 6, pp. 60-61; Table 7, pp. 62-63). The redox potential of the sediments were not measured during the pre-incubation, prior to day 0. The water phases were generally <220 mV, which would be considered a moderately reducing environment (Abiotic Transformations in Water, Sediments, and Soil (N. L. Wolfe, U. Mingelgrin and G.C. Miller, SSSA Book Series, no. 2 -- Pesticides in the Soil Environment, 1990.)
2. Several transformation products were isolated at >10% of the applied but were not identified. RW7 was isolated at 13.2% of the applied from two samples, PW5 was isolated at 20.2 and 21.3% from two samples, and PS4 and PS6 were isolated from individual samples at 10.2 and 16.5% of the applied, respectively (Table 19, p. 75; Table 28, p. 84; Table 32, p. 88).

IV. REVIEWER'S COMMENTS:

1. The TLC methods that were used to separate and characterize [¹⁴C]residues were not clearly described. Some procedures that were discussed in the study results or referred to in the Figures were not described in the methodology.

Eighteen solvent systems were identified in the methodology. Many of these solvent systems do not appear to have been used in this study, but were reported because they were available. In some cases, the only evidence that a specific solvent system was used was that it was referenced on a sample chromatograph.

The study author mentions that some samples were analyzed using RP-18 plates with Solvent Systems 16 and 17. The reason for this alternate approach was not identified. Based on the sample chromatographs, it appears that this is a second analysis system that was used to compare the isolated [¹⁴C]residues to reference standards (Figures 30, p. 125; Figure 33, p. 128).

The study author stated that cochromatography with the reference standards by two-dimensional TLC was not applicable (p. 33, 49). No explanation was provided as to why this procedure for identifying compounds was not applicable, and the sample chromatographs indicate that the samples were cochromatographed with reference standards.

In addition, [¹⁴C]residues were identified only by cochromatography with selected reference standards. A second method, such as HPLC or LC/MS, was not used to confirm the identifications.

2. The samples were chromatographed in a two-dimensional TLC system, and isolated areas of radioactivity were removed and chromatographed in a one-dimensional TLC using solvents that were not used in the two-dimensional system. In the one-dimensional system, some areas of

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radioactivity were found to contain more than one compound. RW6 co-chromatographed with reference compound M8 with two minor unknowns. PS3 co-chromatographed with M8 with two minor unknowns (p. 49). The study author did not comment on the identities of the unknown compounds, or suggest why the two-dimensional TLC failed to adequately separate M8 from other transformation products.

3. The temperature was reported to be $20 \pm 2^{\circ}\text{C}$. USEPA Subdivision N guidelines specify that the experimental temperature should be held constant ($\pm 1^{\circ}\text{C}$).
4. The study author reported that the sterile controls did not remain sterile, but that the microbial population was reduced in comparison to “normal” samples. However, no information was provided to demonstrate that the samples were ever sterile; there was no day 0 microbiological analysis. Also, there was no indication that care was taken to keep the samples sterile, because it did not appear that the air being forced through the samples was filtered to remove airborne biological contaminants. The study author did not provide quantitative data from the plate count analyses of the sterile controls. It did not appear from the study methods that the “normal” samples were ever plated, so it is not certain how the microbial populations in the samples could be compared to determine the populations were reduced.
5. The study author used the optimum fit from a first-order, 1.5-order and second-order kinetic model (not specified) to determine the DT50 and DT90 of fenpyroximate in water and the entire system (p. 38). The DT50 and DT90 in sediment was not determined.

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V. REFERENCES: The following references were cited in the study:

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